

## High Pressure Raman Study of Bromine and Iodine: Soft Phonon in the Incommensurate Phase

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A new phase of solid bromine was discovered at a pressure region above 80 GPa by Raman scattering experiments with a diamond anvil high-pressure cell. This phase was found to be the same as the iodine phase V with an incommensurate structure [Nature (London) **423**, 971 (2003)] which appears between the molecular phase I and the monatomic phase II. In the incommensurate phases of both bromine and iodine, Raman active soft modes were clearly found in the low frequency region. The data suggest that the monoatomic phase II occurs above 30 and 115 GPa for iodine and bromine, respectively.

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Simple molecular solids have been an important subject for high-pressure scientists. Under extreme conditions attained by applying high pressure, the distance between the neighboring molecules becomes comparable to the atomic distance in the molecule. This condition causes various interesting phenomena; the covalent electrons bound in the molecules become delocalized, giving rise to evolutions of electronic states such as the insulator-metal transition. When the inter- and intramolecular distances are identical, we cannot identify the molecules in the solid anymore. Thus, the so-called molecular dissociation is attained, and the monatomic phase is formed.

Up to now, various diatomic-molecular solids such as hydrogen [1–4], oxygen [5–7], nitrogen [8], and halogens (chlorine, bromine, iodine) [9–20] have been investigated under high pressure. Recently, for iodine, a new phase was discovered between the molecular phase I and the monatomic phase II by high-pressure x-ray diffraction study [9]. The intermediate phase V takes an incommensurate structure (Fig. 1), which is approximately formed by modulating the phase-II structure. Although a lot of materials are known to show the incommensurate structures [21], phase V in iodine is intriguing in the sense that it appears just before the molecular dissociation, suggesting that the incommensurate structure is an important key of the molecular dissociation.

In the case of bromine for which the molecular dissociation takes place around 84 GPa [15], the incommensurate phase is expected to exist at very high pressures. In the present work we investigate phase V of bromine as well as iodine with high-pressure Raman spectroscopy which is able to detect the vibrational mode peculiar to the incommensurate structure. These high-pressure Raman experiments allowed us to identify the incommensurate phase V in bromine, to discover a soft phonon mode in phase V for both bromine and iodine, and to recognize the molecular-dissociation process as successive transitions from the commensurate to the incommensurate to the normal phase.

The high-pressure experiments for bromine were carried out using a diamond anvil cell (DAC) with beveled anvils with a 0.1 mm culet. A hole of 0.03 mm in diameter drilled in a preindented tungsten gasket of 0.02 mm thickness served as the sample chamber. Liquid bromine was loaded into the chamber of DAC with a syringe. To avoid chemical reaction, the sample preparation was done in a glove box filled with nitrogen gas. The setup for iodine was essentially the same as for bromine, except that the anvils were of a single culet of 0.3 mm and the sample was powder. No pressure medium was used for both bromine and iodine. Raman spectra were measured in a backscattering geometry with a spectrometer (JASCO NR 1800) equipped with a triple monochromator and a charge coupled device detector. Radiation of 532 nm from a solid-state laser (Verdi2W) was used for excitation of the Raman spectra. The illuminated spot for the Raman measurements was less than 5  $\mu\text{m}$  in size. All the spectra were measured at room temperature. Pressure was calibrated on the basis of the fluorescence of the ruby [22].

Figures 2(a) and 2(b) show Raman spectra obtained for iodine and bromine up to 30 and 108 GPa, respectively. In the pressure region of  $\leq 20$  GPa for iodine and  $\leq 80$  GPa for bromine, the spectra were basically the same as those previously reported [12,18,19]. For both iodine and bromine, we observed the four distinct bands from two librational modes ( $A_g^{(L)}$ ,  $B_{3g}^{(L)}$ ), two stretching modes ( $A_g^{(S)}$ ,  $B_{3g}^{(S)}$ ), and the X band (open circles) which has already been reported for iodine but not yet been assigned [12]. It should be discussed at first that the Raman spectrum drastically changes, and a new Raman band marked with the solid circle grows up at 80 GPa for bromine, and at 23 GPa for iodine. The new bands originate neither from monatomic phase II nor from molecular phase I, because phase II with one atom per primitive unit cell has no Raman band, and phase I has not shown any band in this low frequency region. Furthermore, the pressure at which the new band appears for iodine is consistent with that reported for the

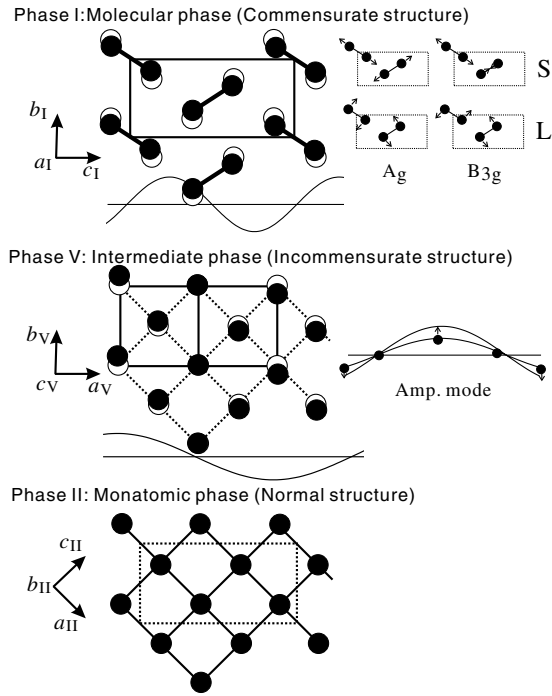


FIG. 1. Crystal structures of three different phases (molecular phase I, intermediate phase V with an incommensurate structure, and monoatomic phase II). The projection of atoms onto the planes indicated is shown. The crystallographic unit cells are shown with solid rectangles. The structure of phase V [9] was interpreted with a face-centered orthorhombic structure modulated with a sine wave; the open circles correspond to the parent structure without modulation (phase II). On the other hand, phase I can be regarded as a commensurate phase if the phase-II structure (the open circles) is taken as the parent structure. Transverse modulation waves for phases I and V are schematically shown below the corresponding structures. In phase I, there are two Raman active stretching ( $A_g^{(S)}$ ,  $B_{3g}^{(S)}$ ) and librational ( $A_g^{(L)}$ ,  $B_{3g}^{(L)}$ ) modes, whose vibrational patterns are indicated.

incommensurate phase V [9]. Consequently, the new Raman bands found in bromine and iodine come from the intermediate phase V with incommensurate structure.

As is well-known, the incommensurate phase always has two types of characteristic vibrational modes, i.e., the amplitude (AMP) mode (the vibrational pattern is schematically illustrated in Fig. 1) and the phase mode [21]. Among them, the former mode is always Raman active because the vibrational motion of the AMP mode preserves the symmetry of the modulation wave [21]. Since only one vibrational band was observed in phase V, the new band can be assigned to an AMP mode peculiar to the incommensurate structure. As can be seen in Fig. 2, the AMP mode (solid circle) was observed simultaneously with the vibrational bands in phase I at 84 GPa (23 GPa) for bromine (for iodine), demonstrating the coexistence of phases I and V. The coexistence of these phases means that the transition between phases I and V is of first order,

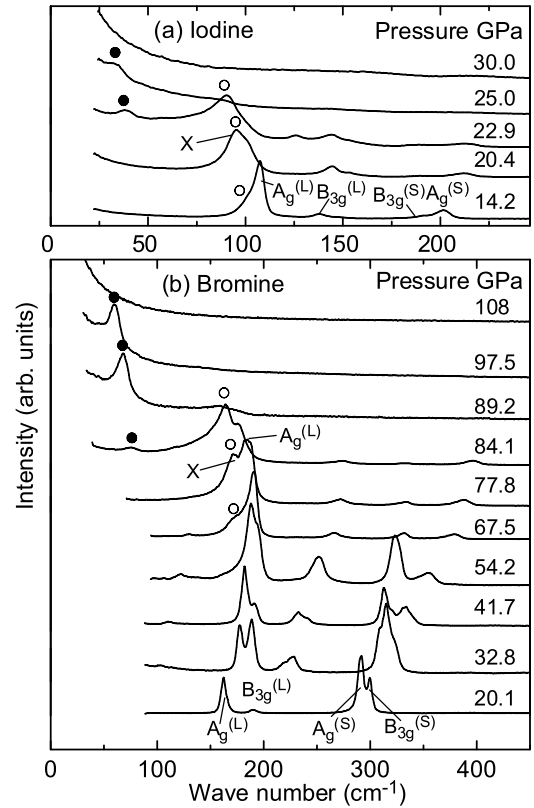


FIG. 2. Raman spectra obtained for (a) solid iodine up to 30 GPa and for (b) solid bromine up to 108 GPa, respectively. Open and closed circles correspond to  $X$  bands in phase I and new bands in phase V, respectively.

consistent with the previous work for iodine. The observed pressure range of coexistence is hatched in Fig. 3.

In Figs. 3(a) and 3(b), the AMP modes are found to show a softening behavior. The monatomic phase seems to be realized at a critical pressure  $P_c$  at which the frequency of the AMP mode becomes zero. In an attempt to estimate  $P_c$ , the pressure dependence of the AMP-mode frequency was fitted by a phenomenological function of  $\omega = (\omega_0^2 - aP)^{1/2}$  [23]. As a result,  $P_c$ 's giving  $\omega = 0$  were estimated to be 31 and 118 GPa for iodine and bromine, respectively. Since the transition between phases V and II is of first order, the phase transition is thought to occur just below  $P_c$ . Indeed, for iodine the transition pressure was reported as 30 GPa [9]. Thus, the transition for bromine is thought to take place around 115 GPa.

Also for phase I, two vibrational bands (denoted with  $A_g^{(L)}$  and  $X$ ) show a softening behavior just before molecular dissociation (Fig. 3). We now discuss the soft mode related with the molecular dissociation. The existence of the soft mode has been suggested by considering the molecular dissociation as a displacive structural phase transition. Taking the structure of phase II as a parent structure, the molecular phase I can be formed by atomic displacements expressed by a modulation wave commensurate with the lattice periodicity of phase II [10,13]. The

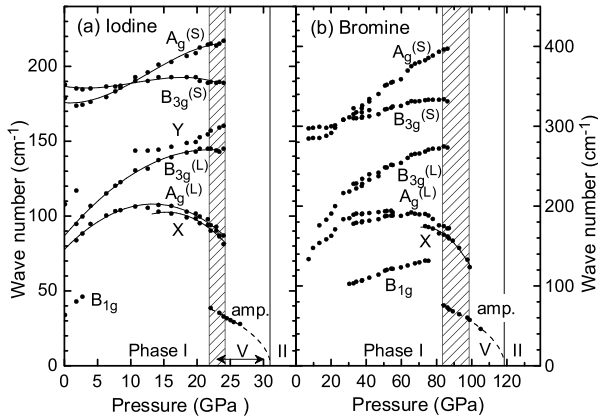


FIG. 3. Pressure dependence of vibrational frequencies of (a) solid iodine and (b) solid bromine, respectively. The solid lines are drawn to guide to the eye. The dashed curves are the results of the fitting with a phenomenological function of  $\omega = (\omega_0^2 - aP)^{1/2}$ . A critical pressure  $P_c$  for  $\omega_0 = 0$  was obtained as 31 and 118 GPa for iodine and bromine, respectively. The obtained fitting parameters  $(\omega_0, a)$  were  $(70.3 \text{ cm}^{-1}, 1.59 \times 10^2 \text{ cm}^{-2}/\text{GPa})$  and  $(139.3 \text{ cm}^{-1}, 1.64 \times 10^2 \text{ cm}^{-2}/\text{GPa})$  for iodine and bromine, respectively. The pressure range of phase V reported in the recent x-ray work [9] is shown with a horizontal arrow in (a). For hatched areas, see the text.

modulation function has been decomposed into two waves [10], that is, a primary transverse wave with  $\mathbf{q} = 1/4(\mathbf{a}_{\text{II}}^* + \mathbf{c}_{\text{II}}^*)$  indicated in Fig. 1, and a secondary longitudinal wave with a wave vector of  $2\mathbf{q}$ , where  $\mathbf{a}_{\text{II}}^*$  and  $\mathbf{c}_{\text{II}}^*$  are the reciprocal lattice vectors in phase II. The phonons corresponding to these modulation waves are the candidates for the soft phonon. Since the eigenvector of the  $A_g^{(L)}$  mode was theoretically predicted to be along the  $b_1$  axis at high pressures [20], the vibrational pattern is seen to be the same as the one of the modulation wave (the transverse wave in the above). Thus, the  $A_g^{(L)}$  mode can be accepted as the soft mode. For the X band which also shows the softening and has not been assigned, the discussion will be made later. It should be noted that both the AMP and  $A_g^{(L)}$  modes can be represented by transverse standing waves with the identical direction of oscillation (Fig. 1). Only the magnitude of the wave vector is different; the AMP mode has the wave vector of, e.g.,  $0.26\mathbf{a}_{\text{V}}^* = \sim 1/8(\mathbf{a}_{\text{II}}^* + \mathbf{c}_{\text{II}}^*)$  at 24.6 GPa for iodine [9], while the  $A_g^{(L)}$  mode has  $1/4(\mathbf{a}_{\text{II}}^* + \mathbf{c}_{\text{II}}^*)$ . Therefore, we conclude that the soft mode in phase V (AMP mode) is essentially the same as that in phase I ( $A_g^{(L)}$  mode).

The above consideration allows us to recognize the molecular dissociation of bromine and iodine to be well-known successive phase transitions [21] from the commensurate (phase I) to the incommensurate (phase V) to the normal (phase II) phase. These types of phase transitions have been reported for a lot of materials including the solid element uranium [24]. However, the present cases of bromine and iodine are still unique in the sense that these types of transitions are found in molecular dissociation of ele-

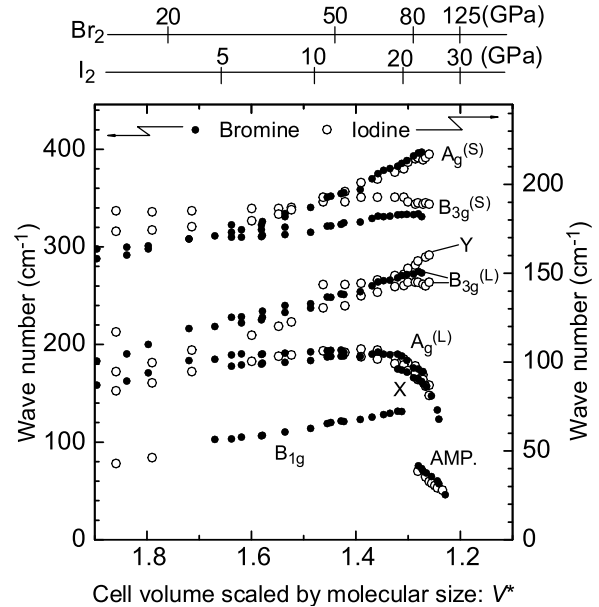


FIG. 4. Vibrational frequency plotted as a function of cell volume scaled with the molecular size. The scaled volume  $V^*$  has been introduced in the previous x-ray work for halogen [15,16] and is defined with  $V^* = V/8r^3$ , where  $V$  and  $r$  are unit cell volume and bond length in the halogen molecule, respectively. The pressure scales for bromine and iodine are indicated for convenience.

ments. As the driving force of the successive phase transitions, a coupling between a charge density wave and a phonon can be considered, as has been proposed by Luty and Raich [13].

We now focus our attention on the similarities between iodine and bromine. Figure 4 shows the Raman frequencies plotted versus a scaled volume  $V^*$  defined with  $V/(8r^3)$ , where  $V$  and  $r$  are unit cell volume and bond length in the molecules, respectively [15,16,25]. If the vertical axis for bromine is scaled by a factor of 1.83 as shown in Fig. 4, all the vibrations, except for the  $B_{3g}^{(S)}$  mode and the Y band, are in approximate agreement with those of iodine. However, the factor of 1.83 cannot be explained by the square root of atomic mass ratio  $(M_{\text{I}}/M_{\text{Br}})^{0.5} = (126.9/79.9)^{0.5} = 1.26$  but deduces the spring constant in bromine being twice larger than in iodine. We also notice that the AMP mode of phase V appears in the range of  $V^*$  from 1.28 to  $\sim 1.20$ . If chlorine also follows this rule, the incommensurate structure is expected to appear from 200 to 300 GPa.

Finally, let us now turn to the Raman spectral changes observed below 80 GPa for bromine. As seen in Fig. 2(b), in the pressure lower than about 20 GPa, we observed four distinct Raman bands (Fig. 1), consistently with the previous Raman experiments [18,19]. However, around 25 GPa, we observed splitting in several peaks. The splitting is obvious for the  $A_g^{(L)}$  mode but is observed also for the other peaks of  $B_{3g}^{(L)}$ ,  $B_{3g}^{(S)}$ , and  $A_g^{(S)}$  modes. The split peaks seem to turn again into one around 60 GPa. Accord-

ing to x-ray absorption studies for bromine under high pressure, changes in the electronic properties were suggested to occur around 25 GPa [26]. Recent extended x-ray-absorption fine structure spectroscopy experiments show an anomaly in the molecular bond length in this pressure region [27]. The present Raman splitting implies some structural changes. Since, however, the previous x-ray studies have reported no structural change [15,16], the possible structure is some weakly modulated structure. Further application of pressure causes the  $X$  band around 70 GPa. The  $X$  band increases in intensity with increasing pressure and suddenly disappears on the transition to phase V. According to the previous electrical conductivity measurements [11,17], metallization for bromine takes place around 60–70 GPa, and for iodine at 16 GPa. The appearance of the  $X$  band seems to be linked with metallization. Although it is still difficult to identify the origin for the  $X$  band and the  $Y$  band, observed only for iodine, the bond charge distortion wave [13], induced by delocalization of the covalent electron, may play an important role for forming the unassigned bands.

In summary, the incommensurate phase V for bromine was discovered just before the molecular dissociation, following that for iodine. A soft phonon mode, peculiar to the incommensurate phase, was clearly found for bromine and iodine. The observation of the soft phonon allowed us to understand the molecular dissociation as a successive phase transition of the commensurate-incommensurate-normal phase. Although a lot of materials show the successive transition, the present case is unique in the sense that it is associated with a molecular-dissociation transition for a solid of a simple molecule. It is desirable that the present observation will motivate further theoretical and experimental investigations, to gain a better understanding of the lattice dynamics and of the way of the molecular dissociation for various other simple molecules such as hydrogen, oxygen, and so on.

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